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Bulletin of Chemical Reaction Engineering & Catalysis, 16 (3) 2021, xxx-xxx

Review Article

Challenges & Opportunities on Catalytic Conversion of Glycerol to Value Added Chemicals

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Received: 23rd March 2021; Revised: 14th May 2021; Accepted: 14th May 2021
Available online: 28th May 2021; Published regularly: September 2021

Abstract

With the rapid expansion of biodiesel industry, its main by-product, crude glycerol, is anticipated to reach a global production of 6 million tons in 2025. It is actually a worrying phenomenon as glycerol could potentially emerge as an excessive product with little value. Glycerol, an alcohol and oxygenated chemical from biodiesel production, has essentially enormous potential to be converted into higher value-added chemicals. Using glycerol as a starting material for value-added chemical production will create a new demand on the glycerol market such as lactic acid, propylene glycol, alkyl lactatehydrogen, olefins and others. This paper briefly reviews the recent development on value-added chemicals derived from glycerol through catalytic conversion of refined and crude glycerol that have been proven to be promising in research stage with commercialization potential, or have been put in a corporate marketable production. Despite of the huge potential of products that can be transformed from glycerol, there are still numerous challenges to be addressed and discussed that include catalyst design and robustness; focus on crude or refined glycerol; reactor technology, reaction mechanism and thermodynamic analysis; and overall process commercial viability. The discussion will hopefully provide new insights on justified direction to focus on for glycerol transformation technology.

Keywords: glycerol; catalytic transformation; value added chemicals; biodiesel

How to Cite: Z.Y. Zakaria, M. Jusoh, S.S. Kader, S.S. Idris (2021). Challenges & Opportunities on Catalytic Conversion of Glycerol to Value Added Chemicals. *Bulletin of Chemical Reaction Engineering & Catalysis*, 16(3), xxx-xxx (doi:10.9767/bcrec.16.3.10524.xxx-xxx)

Permalink/DOI: https://doi.org/10.9767/bcrec.16.3.10524.xxx-xxx

1. Introduction

The notion of catalytic glycerol conversion to important chemicals and fuel is not new [1–3]. Catalytic conversion of glycerol to value added chemicals has emerged as another essential and potential process to be profitable [4]. This occurs in view of the abundant availability and rock bottom price of glycerol in the market [5]. Several reactions involving the catalytic transformation of glycerol to precious chemicals, such as hydrogen [6], acrolein [7], propylene glycol [8], dihydroxyacetone [9], glycerol carbonate [10], epichlorohydrin [11], glycerol ether [12], olefins [13] and others, have been widely reported.

Glycerol is a trihydric compound of three hydroxyl groups that is used in a variety of industrial applications. Along with starch, cellulose, hemicelluloses, and other carbohydrate poly-

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mers, it is a form of monomer found in the majority of natural polyols [14]. Glycerol is primarily generated in the oil and fats industry by high-pressure splitting [15], saponification process to produce soap [16] and production of biodiesel [17]. The processing of biodiesel appeared to be the most important contributing source of glycerol among the three processes. Currently, biodiesel is made by transesterifying vegetable oils (triglycerides) with methanol, yielding 1 mol of glycerol per mol of triglyceride feedstock. The price of glycerol is expected to drop dramatically as biodiesel production increases, compared to the current level, which has already dropped by half in the last few years. Crude glycerol prices have plummeted, although production has risen from 1.16 to 2 Mtons in the EU alone from 2015 to 2017. By 2026, global demand for this chemical is projected to exceed 5 Mtons [18]. The prices of glycerol are around 2000–3000 US$ per ton [18]. Since 2001, the price of unrefined glycerol has dropped by 25–40%, to \$0.35 kg^{-1} to \$0.45 kg^{-1} in 2010 [19]. Glycerol surplus has risen from 200,000 tonnes in 2003 to over 2 million tonnes in 2011, with a forecast of over 6 million tonnes by 2025 [20]. Crude glycerol is the primary by-product of today's biodiesel processes, which use homogeneous acid and simple catalysis. Heterogeneous catalysis, which uses mixed oxides, simple catalysts, and enzymes, produces more pure glycerol [21].

As opposed to hydrocarbons, glycerol has the advantage of being a highly functionalized molecule that can be used as a feedstock for the manufacture of useful products. Glycerol can be biologically and chemically transformed into other useful products [22,23]. Microbial bioconversions is one of the methods for crude glycerol to convert into high value added products that could be used as either end-products or intermediates [24–26]. The use of bacteriologic transformation of glycerol has been confirmed for the manufacture of fuels and chemicals [27,28], the application of cosmetics [27], polyhydroxyacanoate for medical and agricultural field [29] as well as a variety of other items for use in basic chemical applications.

Nonetheless, the ultimate issue is the feasibility of the overall process to be commercially viable. Many of the processes are not in optimum state to be invested on. Aspects such as the fundamental chemistry, catalyst design and stability, process, reactor development, modelling and simulation works are still lacking. More investigations need to be performed to seek and establish a profitable pathway for catalytic conversion of glycerol to its derivatives. The objective of this mini review is to examine the available processes for catalytic conversion of glycerol to important chemicals with consideration of utilizing refined and crude glycerol. Associated features within the processes such as catalyst selection, process parameters, reactor selection, feasibility study and economic potential are detailed out. Finally, discussion on the challenges, opportunities and direction follow.

2. Catalytic Conversion of Refined and Crude Glycerol to Value-added Chemicals

The catalytic transformation of refined glycerol to value added chemicals have been explored since mid-1990s [30–34]. The research trend since then has vigorously expanded to the present time, especially with the rapid progress of the biodiesel production worldwide. Since the value of glycerol keeps declining over time, it is indeed imperative to valorise glycerol and this can be done by converting it into chemicals of higher value and importance. Table 1 and 2 tabulate several selected important chemicals that have been converted from refined and crude glycerol recently. The forthcoming discussion will be closely linked to these tables. Refined glycerol is chosen due to its purity and for investigation purposes on the feasibility of the glycerol conversion. Having less parameter (impurities in crude glycerol) to concern will enable focus on the chemistry of the catalyst, reaction, process parameters and optimization.

Glycerol carbonate is one of the important derivatives of glycerol [35] and this is reflected from its USD\$3000–3400/tonne price tag [36]. It has versatile reactivity due to the presence of a hydroxyl group and a 2-oxo-1,3-dioxolane group which manage to initiate enormous applications in various domains from polymers to solvents [37]. Several routes to obtain glycerol carbonate from refined glycerol include transesterification [36,38,39], carboxylation [40] and carbonylation [41]. Among cheaper options to derive glycerol carbonate is mixing it with sodium bicarbonate over natural Clinoptilolite in a 500mL batch reactor. The natural Clinoptilolite was successfully upgraded to a two dimensional zeolite solid acid catalyst with properties mimicking topology of the HEU framework in a work by Mahdi *et al.* [40]. Effect of temperature, catalyst mass, catalyst diameter, glycerol solvent ratio, sodium bicarbonate to glycerol ratio and reaction time were evaluated comprehensively. Evidently, the optimum conditions were attained at glycerol: sodium bicarbonate:

Table 1. Catalytic conversion of refined glycerol to value added chemicals.

Products	Reactions	Reactants	Operating Conditions	Catalyst	Performance	Ref
Glycerol carbonate	Carboxylation	Refined glycerol $NaHCO_3$	Stirring rate= 600 rpm; t=90minutes; T = 60-100 ^oC; Solvent ratios=3–7 mol water; Conc. of catal.=1–9 wt%; Catal. dia.=0.46–0.91 mm	Natural clinoptilolite Dealuminated clinoptilolite	After 10 minutes: C_g = 10% C_g = 29%	[40]
Glycerol carbonate	Carbonylation Photo-thermal at visible light	Refined glycerol CO_2	T=150^{o}C; t= 6 h; P=8 MPa CO_2; RG=10 mmol; DMF= 20 mL; Visible light irradiation = 250W; Catal. Mass=1.0 g	$ZnWO_4$-ZnO Au/$ZnWO_4$-ZnO	Y=10.6%	[41]
Aromatics (BTX)	Aldol condensation Oligomerization-decarbonylation	Refined glycerol Methanol	T=400 ^{o}C t=2.5 h P=1 atm WHSV= 1.07h^{-1} Catal. mass = 1.6 g	HZSM-5 Zn/ZSM-5 (0.64 wt.%) Mo/ZSM-5(0.65 wt%) Sn/ZSM-5 (0.66 wt.%) Ni/ZSM-5 (0.65 wt.%) Ag/ZSM-5(0.63 wt.%) Sn/ZSM-5 (2.34 wt.%)	Y_{BTX} = 13.9% Y_{BTX} = 20.1% Y_{BTX} = 16.5% Y_{BTX} = 17.9% Y_{BTX} = 16.1% Y_{BTX} = 14.2% Y_{BTX} = 21.1%	[48]
Aromatics (BTX)	Deoxygenation Dehydration	Refined glycerol Methanol	T=400 ^{o}C P=1atm Catal. mass=1.6 g Catal. size=40-60 mesh Glycerol conc.=40% WHSV=0.71 h^{-1}	HZSM-5 0.3M NaOH/HZSM-5 0.3M CH_3ONa/HZSM-5 0.3M TPAOH/ HZSM-5 0.3M TMG/ HZSM-5 0.3M $NaHCO_3$/ HZSM-5 0.3M NH_4OH/ HZSM-5	C_g=100%; Y_{BTX} =24.5% C_g = 100%; Y_{BTX}=28% C_g = 100%; Y_{BTX}=29% C_g = 100%; Y_{BTX}=27% C_g = 100%; Y_{BTX}=26.5% C_g = 100%; Y_{BTX}=25% C_g = 100%; Y_{BTX}=25%	[50]
Propane	Dehydration, dehydrogenation, hydrogenation	Refined glycerol, hydrogen	T=543 K t=12 h P=2 MPa Carrier gas=H_2/N_2 *Argon/N_2 was used **1,2-propanediol was used, not glycerol, for comparison.	Pt/H-ZSM-5 (29) Pt/H-ZSM-5 (29)* Pt/H-MOR (18.3) Pt/γ-Al_2O_3 Pt/USY (6.3) Pt/Beta (27) Pt/SiO2 Pt/H-ZSM-5 (29)** Pt/γ-Al_2O_3 **	C_g=80.2%; S_{C3H8}=35.4% C_g=35.7%; S_{C3H8}=7.15% C_g=79.6%; S_{C3H8}=30.4% C_g=77.4%; S_{C3H8}=13.3% C_g=47.3%; S_{C3H8}=18.9% C_g=12.1%; S_{C3H8}=13.2% C_g=5.13%; S_{C3H8}=20.3% C_g=70.7%; S_{C3H8}=35.8% C_g=79.6%; S_{C3H8}=36.1%	[53]
Olefins (ethylene, propylene, butylene)	Dehydration, dehydrogenation	Refined glycerol	T=650^{o}C; t= 0.5 h; P=1 atm; Gly. Conc=26.91%; WHSV=116.54 h^{-1}	Cu/ZSM-5	C_g = 100%; S_{Ole}= 20.5%; Y_{Ole}= 16.4%	[13]
Ethers (mono-benzyl-glycerol ether $_{(MBG)}$; di-benzyl -glycerol ether $_{(DBG)}$; dibenzyl ether$_{(DBz)}$)	Etherification	Refined glycerol Benzyl alcohol	Catal. mass=50 mg Stirring=8-15 hours T=120-140 ^{o}C	Z15c Z40c Z40c-H	C_g = 77%; S_{MBG}= 61% S_{DBG} = 38%; S_{DBz}= 3% C_g = 76%; S_{MBG}= 28% S_{DBG}= 60%; S_{DBz}= 11% C_g = 70%; S_{MBG}= 14% S_{DBG}= 68%; S_{DBz}= 18%	[58]
Solketal	Acetalization	Refined glycerol Acetone	T=343 K Molar ratio glycerol to acetone =1:1.	MFI-1-CA MFI-2-CA BEA-CA MOR-CA	C_{Glu}=82%; $S_{Solketal}$~ 100% C_{Gly}=85%; $S_{Solketal}$~ 100% C_{Glu}~84%; $S_{Solketal}$~ 100% C_{Gly}~79%; $S_{Solketal}$~ 100%	[59]
Ethyl lactate$_{(EL)}$ Solketal$_{(SK)}$	Acetalyzation	Glycerol (99%) DHA Decane EtOH	T=90 ^{o}C t=24 h Revolution= 1200 rpm	Sn-NTs Sn-NTs-A, Sn-NTs-B	Y_{EL} = 0%; Y_{SK} = 0% Y_{EL} = 13%;Y_{SK} = 58% Y_{EL} = 34%	[60]

Gly = glycerol; BTX = Benzene, toluene, xylene; DHA = Dihydroxyacetone; C_g= Conversion glycerol; Sn-NTs-A = Sn Silica nanotubes; Ole=Olefins; Y=yield; Catal=catalyst

water molar ratio 3:1:3. In addition, the best catalyst concentration was 9 wt% and diameter 0.46 mm was acquired at 100 °C. The conversion of glycerol depended heavily on the catalyst activity in promoting reaction, as the operating temperature was just 100 °C and below. It is worth noting that this study is by far more economical than the carbonylation of glycerol to glycerol carbonate via photo thermal reaction using $ZnWO_4$-ZnO and Au/$ZnWO_4$-ZnO catalyst [41]. The introduction of pressure, longer duration of catalytic testing and pricier catalyst may be a debatable point, but the technique employing powerful synergistic photo-thermal effect introduced a new dimension for the glycerol conversion application. This is a debut scholarly study involving thermal-driven catalytic system applied as driving force for the direct synthesis of glycerol carbonate.

Regardless of the above findings, the success of getting glycerol carbonate from crude glycerol could be more exciting as the feed is significantly cheaper, thus could reduce production cost. Qing and co-worker used a simple set up to trans-esterify crude glycerol with dimethyl carbonate over 1,8-diazabicycloundec-7-ene (DBU) catalyst and obtained crude glycerol conversion of 90% and selectivity of 89%. Upon upgrading the catalyst from DBU to DBU/glycerol/CO_2 (DGC), the result obtained was not attractive. The study actually intended to utilize crude glycerol that contains DBU and DGC as impurities. In order to develop a biodiesel production technology catalyzed by DBU, the utilization of residual DBU and DGC in crude glycerol as catalysts to convert glycerol and DMC into GC under mild conditions were carried out. As far as it is concerned, this is the first study that utilizes the impurities in crude glycerol as a source of catalyst [36]. Another modern approach to derive glycerol carbonate is via a microwave assisted transesterification reaction over calcium oxide catalyst. Astonishing results were obtained upon studying various crude glycerol concentration feed over the catalyst. Ironically, crude glycerol of 70% purity yielded the best result compared to a better quality crude and refined glycerol, as shown in Table 2. The findings pointed out that impurities in crude glycerol strangely but positively affects the transesterification of glycerol to glycerol carbonate via the utilization of microwave reactor.

Catalytic glycerol transformation to aromatics, particularly benzene, toluene and xylene (BTX) recently draws great attention [42]. Aromatics are conventionally derived from the catalytic reforming of naphtha in a petroleum refinery [43]. Ability to decrease dependency on fossil source by glycerol transformation to BTX is deemed as very attractive. Benzene is used for the process of cumene to phenol and ethylbenzene to styrene as well as the production of cyclohexane [44]. Toluene is used in refinery streams such as gasoline blending for its octane value [45] whereas xylenes may either be used in refinery streams for gasoline blending or further separated by isomers for chemical applications [46].

Zeolites ZSM-5 is the most popular catalyst for the conversion of glycerol to aromatics [47]. Wang and co-worker modified zeolite ZSM-5 catalyst and postulated that there are two main routes in the glycerol to aromatics process. The first route is the aldol condensation of glycerol dehydration, whereby oxygen in the glycerol is removed in the form of H_2O, while the second path is via olefins oligomerization that originates from the decarbonylation of glycerin dewatered products, whereby oxygen is detached from the feed in the form of CO or CO_2 [48]. He discovered that 2.34 wt% Sn/HZSM-5, produced 21.1 wt% BTX aromatics yield in a space of 10 h catalyst lifetime, which is the best screening result they gained. Further upgrading of the catalyst produced 25.2% aromatic yield. The phenomenon is explained by the incorporation of Sn cations that favourably quickens the decarbonylation steps of acetone to butene, and subsequently, assists the formation of xylene aromatics [48].

Desilication of HZSM-5 catalyst with alkali directly modifies the intramesoporosity and microporosity that can affect to aromatics formation from glycerol via consecutive deoxygenation and dehydration reactions [49]. This resulted in higher aromatics yield that not only include BTX but, trimethylbenzene and tetramethylbenzene. Notable discovery from this includes that intramesopores with size ranging between 3–5 nm and well-preserved parent HZSM-5 microporosity displayed better shape-selective BTX yields and gentler carbon deposition rate compared to the bigger size of 6–16 nm in the glycerol transformation [50]. In a separate study, Wang investigated on the effect of acid site density on a dealuminated ZSM-5 catalyst for glycerol conversion to aromatic using liquid and gas route. A mild HNO_3 treatment was applied and it preferentially eradicates the non-shape selective acid sites from HZSM-5 framework, promoting aromatics formation. Dealuminating the catalyst, on the other hand, transformed the framework tetrahedral of HZSM-5 Al species into EFAl species, promoting the decrease in the aromatics yield.

Table 2. Crude glycerol catalytic conversion to value added chemicals.

Products	Reactions	Reactants	Operating Conditions	Catalyst	Performance (%)	Ref
Glycerol carbonate (GC) Glycidol (Gy)	Transesterification	Crude glycerol Dimethyl carbonate	DMC-to-glycerol Molar ratio =3:1 4.0% DBU wt.% t=60 min T=40 °C	1,8-diazabicycloundec-7-ene (DBU) DBU/glycerol/CO_2 (DGC)	C_g= 90% S_{GC}=89% S_{Gy}=11% C_g= 23%	[36]
Glycerol carbonate (GC)	Transesterification	Refined glycerol, Crude glycerol, Dimethyl carbonate (DMC)	Microwave assisted process T=65 °C t=45min Catal. loading=6 wt.% DMC:Gly=2:1 3 types of glycerol: 99%, 86%, 70% purity.	Calcium oxide	$C_{G\ 99\%}$= 38% Y_{GC}=45% $C_{G\ 86\%}$= 5% Y_{GC}=20% $C_{G\ 70\%}$= 75% Y_{GC}=79%	[39]
Aromatics-BTX	Pyrolysis, Dehydrated to oxygenate, aldol condensation, dissociation, cyclization, oligomerization, Aromatization	Crude glycerol	T=500 °C (pyrolysis) T=550 °C (upgrading) P=1 atm Catal. size=1-2 mm Catal. Mass=200 g	ZSM-5 (MFI)(23)	C_g = 100% $S_{Benzene}$ = 27%, $S_{Toluene}$ = 45% S_{Xylene} = 28%. 11 regeneration cycles. After 11 regeneration activity dropped to 95%.	[52]
Propylene	Hydrogenolysis, Cracking	Crude glycerol	T=523K 59 wt.% glycerol WHSV=1 h^{-1} TOS= 2 h H_2/gly=100	Ir/ZrO_2&ZSM-5-30 WO_3 + Cu/Al_2O_3&ZSM-5-30 Pt-HSiW/ZrO_2&ZSM-5-30 ReOx + Ir/Al_2O_3&ZSM-5-30 ReOx + Rh/Al_2O_3&ZSM-5-30 MoO_3 + Ni_2P/Al_2O_3&ZSM-5-30 MoO_3 + Ni_2P/Al_2O_3&ZSM-5-30 MoO_3 + Ni_2P/Al_2O_3&ZSM-5-127 NaCl + Ni_2P/Al_2O_3&ZSM-5-127 KOH + Ni_2P/Al_2O_3&ZSM-5-127	C_G= 72% S_{C3H6}=85% C_G= 87% S_{C3H6}=82% C_G= 92% S_{C3H6}=81% C_G~100% S_{C3H6}=86% C_G~100% S_{C3H6}=85% C_G~100% S_{C3H6}=88% C_G~100% S_{C3H6}=46% C_G~100% S_{C3H6}=72% C_G~100% S_{C3H6}=74% C_G~100% S_{C3H6}=74%	[55]
1,2-propanediols 1,3-propanediols	Hydrogenolysis	Refined glycerol Crude glycerol Hydrogen	T=200 °C T=24 h P=3.4 MPa Gly/catalyst ratio 12:1 w/w 250mm stirring 4 generation cycles tested	HDT-Fe-7 (RG) HDT-Ni-7 (RG) HDT-Cu-7 (RG) HDT-Zn-7 (RG) HDT-Cu-15 (RG) HDT-Cu-15 (CG)	C_g = 50.6% S_{Acetol}=100% C_g = 47.8% $S_{1,2\text{-PDO}}$=100% C_g = 66.0% $S_{1,2\text{-PDO}}$=95.7% C_g = 0% $S_{1,2\text{-PDO}}$=0% C_g = 89.7% $S_{1,2\text{-PDO}}$=92.0% C_g = 97.2% $S_{1,2\text{-PDO}}$=74.1%	[62]

Table 2. (Continued…)

Products	Reactions	Reactants	Operating Conditions	Catalyst	Performance (%)	Ref
Solketals: 4-hydroxymethyl-2, 2-dimethyl-1,3-dioxolane	Acetalization	Crude glycerol Acetone	T=40 °C, t=90 min, MR Ac/Gl=10/1, Catal =10 wt% T 20 °C, t=90 min, MR Ac/Gl=10/1, Catal=10 wt% T=40 °C, t=90 min, MR Ac/Gl=1/1, Catal=10 wt%	HR/Y-W20 HR/Y-W20 HR/Y-W20	C_g= 100% $S_{Solketal}$=97.85% C_g= 93.6% $S_{Solketal}$=65.36% C_g= 99.5% $S_{Solketal}$=95.15%	[98]
Hydrogen	Photoreforming	Refined glycerol Crude glycerol	Untraviolet, 20 vol% RG, volume 300 mL, Ultraviolet, 1 vol% GC, volume 300mL. Visible light, 20 vol% RG, volume 300 mL	TiO_2/rGO(3%)/Pt(3.8%)	H_2 produced: 70.8 mmol $h^{-1}g^{-1}$ 12.7 mmol $h^{-1}g^{-1}$ 3.3 mmol $h^{-1}g^{-1}$	[65]
Hydrogen	Steam reforming Water	Crude glycerol	T=650 °C P=1 atm Catalyst=0.2 g #Conversion at t=1 h	Ni/AC NiY/AC NiLa/AC NiMg/AC Rh/NiMg/AC	C_G= 75%# Y_{H2}=44% C_G= 78%# Y_{H2}=80% C_G= 80%# Y_{H2}=81% C_G= 86%# Y_{H2}=85% C_G= 96%# Y_{H2}=89%	[63]
Hydrogen	Partial oxidation steam reforming Autothermal reforming	Synthetic crude glycerol	S/C =2.6 O/C =0.50 T=500 °C T=550 °C T=600 °C T=650 °C W/FA0=127.4 gcat.min/mol.C	5Ni/CeZrCa	 C_G=60% S_{H2}=48% C_G=82% S_{H2}=67% C_G=90% S_{H2}=68% C_G=91% S_{H2}=70%	[6]
Hydrogen	Steam reforming	Crude glycerol	P=1 bar GHSV=20 $L.h^{-1}.g^{-1}$ $WHSV_{CG}$= 3 h^{-1} TOS=10 h Catal. mass=0.2 g	NiLaTi700 NiLaTi850	Reaction T=500°C C_G=99.5% S_{H2}=57.1% C_G=99.7% S_{H2}=66.3% Reaction T=650°C C_G=99.3% S_{H2}=55.8% C_G=99.5% S_{H2}=66.4%	[64]

C_G= Conversion glycerol; RG = run with refined glycerol; CG = run with crude glycerol; $S_{1,2\text{-}PDO}$ = Selectivity to 1,2-propanediols; S_{GC}= Selectivity glycerol carbonate; Y_{GC}= Yield of glycerol carbonate; Catal = catalyt.

On a different note, a sequential steaming and leaching treatment created an intramesopore structure within the framework that managed to improve the life span of the HZSM-5 catalyst up to 11.5 hours by restraining non-shape selective catalytic side reactions and coking [49]. This is an important achievement as other catalysts subjected to this process can last about 3 to 5 hours only [51].

In another research performed by Songbo, crude glycerol was used as reactant in a continuous micro reactor for the production of aromatic BTX over ZSM-5/bentonite extrudates catalyst. The important results from this study are presented in Table 2. This study is comparable to Wang's study [49] in terms of the activity of the catalyst that can remain active up to 4.7 hours, but the plus point here is that Songbo used crude glycerol [52]. The activity of the catalyst is shown to be a function of time which means the percentage BTX yield will be reduce with time due to the development of coke that covers the active site of the catalyst. Regeneration of the catalyst will recover 95% of the initial catalyst activity but after 11 consecutive regenerations step, the yield of BTX drastically dropped to 5.4%. Removal of coke during catalyst regeneration was carried out using an oxidative treatment. An exchange of cations and protons from bentonite and crude glycerol plus ZSM-5 catalyst, respectively could be the reason for a permanent deactivation as the collapse of bentonite layered structure [52].

Propane, a highly important hydrocarbon source, could be obtained catalytically from glycerol via a series of dehydration, dehydrogenation, and hydrogenation reaction with hydrogen as a co-feed when subjected to various platinum impregnated zeolite catalysts. Among all catalyst, Pt/HZSM-5 showed most promising outcome with the highest glycerol conversion (80.2%) and propane selectivity (35.4%). Stronger acid site on the catalyst surface promotes the formation of more intermediates via the dehydration reaction compared to the steam reforming route. These intermediates are then subjected to hydrogenation reaction ought to the presence of Pt/H_2 to form subsequent intermediate together with methane and ethane. Repeated dehydration and hydrogenation finally leads to the formation of propane, a more stable product than the other intermediates [53]. The overall equation of the reaction is as per shown in Equation (1), where hydrogen is an essential co-feed to produce propane.

$$5C_3H_5(OH)_3 + 5H_{2\,(g)} \rightarrow 4C_3H_8 + 9H_2O + 3CO_2 \quad (1)$$

Since hydrocarbon in the form of methane, ethane, propane can be formed as mentioned earlier, its neighbouring family, alkene (olefins) can also be formed [19]. Modified zeolite ZSM-5 based catalyst with numerous metals were synthesized and subjected to refined glycerol (30% concentration) via steam reforming at 650 °C, 30 minutes, 1 atm and WHSV of 107 h^{-1}. The screening experiment revealed that Cu/ZSM-5 was the best catalyst among other metal ZSM-5 and a process optimization via response surface methodology proceeded afterwards. Optimization of the process showed that selectivity towards olefin (ethylene, propylene and butylene) was 20.5% and the yield was 16.4% [13]. The steam reforming process involves several dehydration and dehydrogenation reactions taking place on the Brönsted / Lewis acid site of Cu/ZSM-5 [54].

Propylene has proven to be able to be produced using crude glycerol as well. Various combinations of metal and acid catalysts were synthesized as per shown in Table 2. Among all, the complex MoO_3 + Ni_2P/Al_2O_3 & ZSM-5-30 emerged as the best catalyst, with selectivity of 88% towards propylene via a two-step systematic process-glycerol hydrogenolysis to propanol followed by propanol cracking to propylene [55]. This could be an excellent approach towards a feasible cost-effective strategy for the commercialization of bio-based propylene.

Ethers is a class of important organic compounds that contain an ether group in which an oxygen atom is connected to two alkyl or aryl groups [56]. Examples of ethers include mono-benzyl-glycerol ether, di-benzyl-glycerol ether and dibenzyl ether which could be catalytically converted from glycerol via etherification process coupled with a co-feed compound [57]. Gonzales studied the Si/Al ratio and the role of mesoporosity in the etherification of refined glycerol with benzyl alcohol over zeolite ZSM-5 catalysts [58]. It was discovered that mono-benzyl-glycerol ether (MBG) was largely produced when low Si/Al zeolite catalyst was used while di-benzyl-glycerol ether (DBG) was the major product over a high Si/Al zeolite catalyst. This indicated that the selectivity towards desired specific ethers can be controlled through the adjustment of Si/Al molar ratio of the zeolite catalyst [58].

Solketal, another important derivative from glycerol can be obtained from the acetalization reaction of glycerol with acetone over hierarchical zeolites (MFI, BEA, and MOR) at 343 K using a 1:1 molar. MFI hierarchical zeolites gave the best glycerol conversion and nearly

100% selectivity to 4-hydroxymethyl-2 and 2-dimethyl-1,3-dioxolane, both that are known as solketal. This occurred due to the convenient access of reagents to the active sites because of the establishment of mesopores structure that appeared from the desilication of the microporous zeolites [59].

Solketal can also be produced via a highly active nanotube where Sn is isomorphically substituted inside the Silica framework. The Sn/silica nanotubes efficiently catalysed the conversion of dihydroxyacetone to ethyl lactate and the transformation of glycerol to solketal [60]. This result is attributed to the improved accessibility of the active sites ascribed to tubular morphology and to the proper combination of acid sites [60]. The active sites are imperative as it hosts numerous types of Bronsted acid on the catalyst surface active site which is vital for glycerol acetalization with co-feed acetone [61]. Manjunathan stressed that strong to weak acidity available in the catalyst correlates to the yield of solketals [61].

Glycerol can be catalytically transformed into 1,2-propanediols and 1,3-propanediols via hydrogenolysis process over various modified metal hydrotalcites. In a work by Lopez *et al*., initially, all catalysts were screened using refined glycerol. The best catalyst, HDT-Cu, was used for further testing of hydrogenolysis with crude glycerol and percentage yield for 1,2-propanediols obtained was 74.1% when the crude glycerol purity used was 62%. This result was obtained when co-feeding the reaction with hydrogen at pressure = 3.4 MPa, temperature = 200 °C in a one day reaction. Regeneration study conducted showed that the catalyst can be used up to 4 times before the activity sharply drops [62].

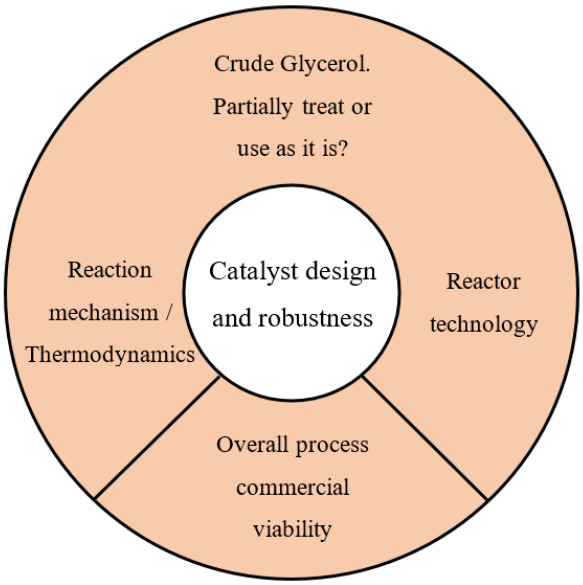

Figure 1. Challenges to be dealt with for catalytic conversion of glycerol to value-added chemicals.

Hydrogen is well known to be attained from glycerol via various reforming processes. A few recent researches utilized crude glycerol for steam reforming [63], partial oxidation steam reforming [64], photo reforming [65] and autothermal reforming [6], as described in Table 2. The glycerol photo reforming offers several advantages such as the utilization of natural free light to excite the reaction and the novel TiO_2/rGO/Pt catalyst for the production of hydrogen. However, the amount of hydrogen produced from the photo reforming reaction is too minute, which means there are plenty of opportunities for this research to be further developed. Nevertheless, most of the hydrogen derived from glycerol via the reforming processes display encouraging results. But the main problem lies in the life span of the catalyst because it deactivates rapidly upon a mere few hours of reaction. This is indeed the main challenge for hydrogen production from catalytic transformation of refined and crude glycerol.

3. Challenges of Catalytic Conversion of Glycerol

The transformation of glycerol (crude or pure condition) to value added chemicals is not easy as it sounds. There are numerous parameters that need to be considered, optimized and obliged. Even though vigorous researches have been conducted since the past decade, overall yield of value added products are still yet to reach pilot or commercial scale accept for few chemicals like epichlorohydrine (ECH) and glycerol carbonate. These are the main challenges that need to be addressed. Subsequently there will be opportunity for improvement of the process so we can head towards the correct direction.

There are several areas that can be focused to rapidly improve the transformation of glycerol to value added chemicals (Figure 1). A significant challenge falls in the decision to select between the utilization of crude or refined glycerol. Both has its own pro and cons. Obviously opting for crude glycerol will be economical on the front end but more complex and costly during reaction and separation stage. Hence, massive research opportunities to seek for a proven reaction or process that can utilize crude glycerol are openly available.

One of the prime areas to improve is the catalyst design and robustness. The catalyst design will have to consider whether crude or

refined glycerol is employed. The physicochemical properties of the catalyst and its reactivity during reaction will affect the rate of deactivation. Hence, this is the reason main focus should be driven to catalyst design. The reactor technology will also be the next issue to be concentrated on. Different value added chemicals require different processes and reactors. One of the lacking elements for the glycerol conversion research is that, less attention are given on the reaction mechanism and thermodynamic modeling of a particular reaction. This indicates that less fundamental reaction and thermodynamic aspects are comprehended. Lacking in this area will halt the progression of upcoming development. Subsequent sub-sections will detail out all points revealed above.

3.1 Catalytic Crude Glycerol Utilization – Partially Treat or Use as It Is?

Distinctive challenges can be viewed from the catalytic transformation of glycerol to value added chemicals. These thermochemical con-

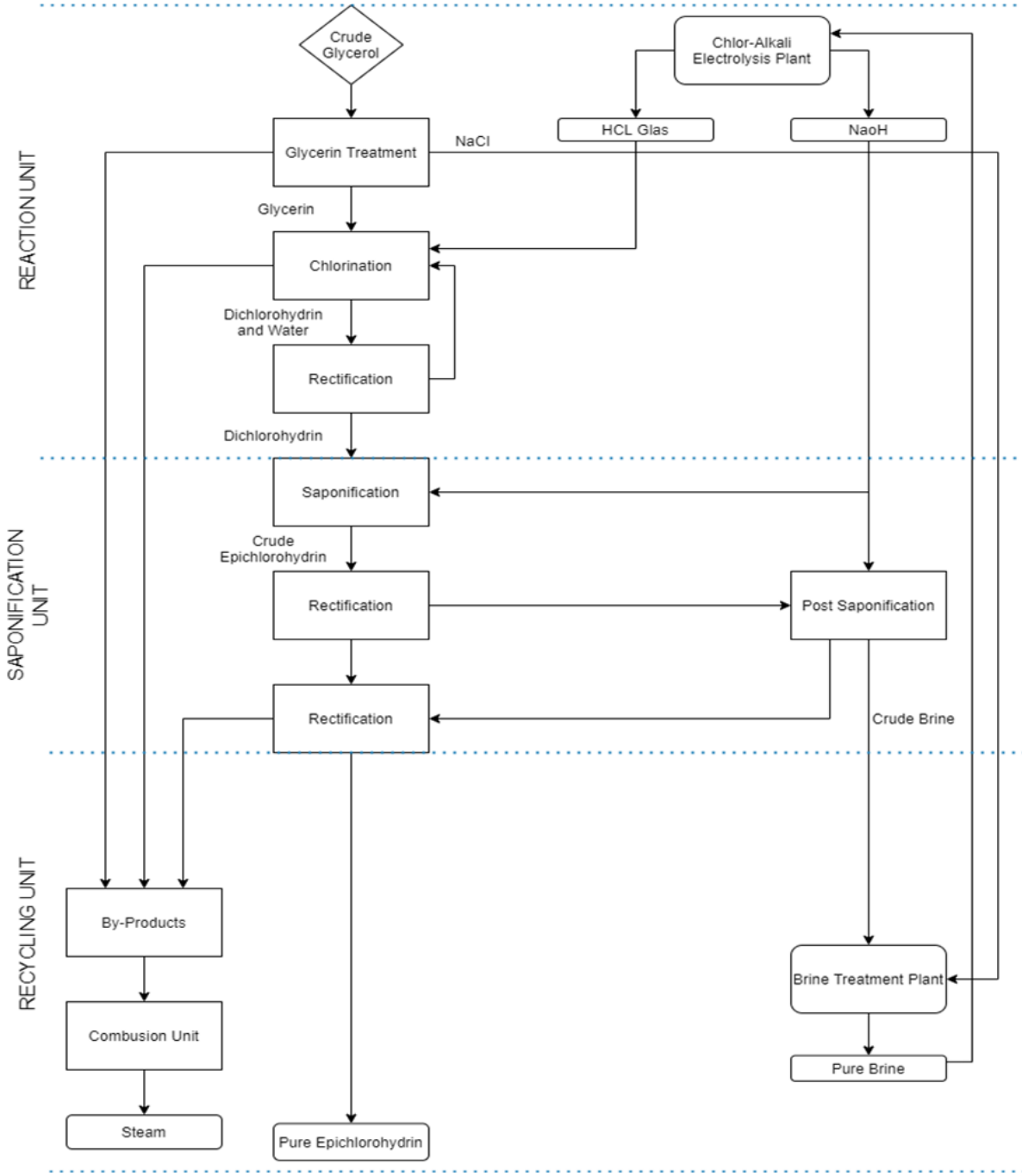

Figure 2. Process overview of Solvay ECH plant showing that crude glycerol needs to undergo treatment prior to further processing [69].

version pathways presently are more complicated than its biochemical conversion counterpart. The price tag difference between crude and refined glycerol is enormous. The cost of crude glycerol is between $0.09 to $0.20 per kg [22]. It will cost $1000 per 200-400 metric tonnes to purify crude glycerol [62]. Hence, economically, it will be more alluring to utilize crude glycerol as feed, due to the cheaper feedstock. Unfortunately, impurities contained within crude glycerol are something that needs to be accepted and dealt with. The quality within the crude glycerol is very subjective and must be carefully tackled. There are two approaches that can be used which are (a) to slightly improve and control the amount of impurities in such a way that the process can accept certain level of undesired compounds; and (b) to have a technology that can directly consume the crude glycerol as it is.

Recent report suggest that the presence of impurities are acceptable for certain process and products [66]. It is hypothesized that steam reforming, dehydration and hydrogenolysis have the potential to consume crude glycerol as reactant at high temperature and pressure [11]. But this remains as a postulated idea as for now. Perchance, a minimum specification requirement for crude glycerol ought to be established for the above mentioned process. Hypothetically, water and methanol in crude glycerol as feed encourage steam reforming but other undesired impurities may contribute destructively. Linde's technology which commenced in 2009 does not directly consume crude glycerol [67]. The impure glycerol reactant is reprocessed, pyrolyzed and reformed, producing a methane-rich gas that is fed into an existing hydrogen plant for purification and liquefaction of hydrogen. The glycerine used in the process is distilled to remove water and salts before it is cracked under high temperature and pressure to produce the pyrolysis gas [68]. This evidently infers that the crude glycerol undergoes certain level of purification before being subjected as reactant to produce hydrogen.

The commercialized ECH process demonstrates similar idea that crude glycerol needs to be treated. This technology to produce ECH epicholohydrin has successfully reached the maturity and commercial viability. Companies such as Solvay and Glaconchemie, not only have the know-how on the technology but are also dedicated to produce sustainable green solvent from glycerine [69]. The ECH process as illustrated in Figure 2 shows that the crude glycerol consumed undergoes specialized treatment process before being sent to the subsequent chlorination stage [69]. This indicates that the crude glycerol goes through some form of purification process, presumably up to a certain purity, that involves cost which can be tolerated within the business perspective.

The crude glycerol at its original nature maybe suitable for processes such as combustion (complete oxidation), gasification (partial oxidation) and pyrolysis (thermal degradation without oxygen) where the biodiesel waste biomass can be processed right away to produce liquid bio-oil [70]. In gasification processes, crude glycerol was adopted and hydrogen was attained [71,72]. Pyrolysis on the other hand offers incredible alternative in the production of liquid bio-oil, solid char and syngas [73,74]. Pyrolysis products can be precious compounds and chemicals. Investigation conducted by Songbo *et al.* [52] obtained 64.0 wt% of liquids (aqueous and oil phases) from pyrolysis of crude glycerol with half of it constituted to BTX aromatics, which indicated that crude glycerol catalytic transformation via pyrolysis can be directed to specific desired chemicals, depending on the catalyst design. In another case, impurities in crude glycerol produce encouraging outcome towards the formation of glycerol carbonate under microwave irradiation, compared to other types of glycerol transformation processes [39]. This means that the impurities positively affect the reactions and somehow increase the product yield. However, the subsequent main struggle lies in the challenge to separate the various precious products. This will indeed be another point of important discussion.

Several chemicals such as 1,2-propanediol, acrolein, dihydroxyacetone, glyceric acid, glycerol ethers, triacetin (glycerol esters) are not yet catalytically feasible at the moment [11] regardless of the issue of utilization of original state of crude glycerol or partially purified crude glycerol. Some of the chemicals, such as acrolein, even when refined glycerol is employed as reactant, the product selectivity and yield are still unpromising [75]. Hitches in percentage product selectivity and catalyst stability must be tackled first. This will be discussed in the subsequent sub-topic of this paper.

In brief, application of crude glycerol as feed depends heavily on the process technology. Some requires some kind of partial purification for further processing. In other contexts, crude glycerol without any prior treatment, is suitable for several thermochemical processes such as pyrolysis. Precious chemicals such as syngas, bio-oil and BTX aromatics are among im-

portant products that can be achieved from crude glycerol without prior treatment. Further research must be conducted to improve the economics of employing crude and partially treated glycerol.

3.2 Catalyst Design and Robustness?

To reach high yield of desired chemicals, catalyst must be accurately designed and operating conditions should be appropriately configured [76]. This is crucial to increase the lifetime and efficiency of the catalyst. The research outcomes pointed out that direct glycerol thermochemical reaction is technologically feasible but hindered by catalyst coking that will poison the catalyst [77] and ineffective catalyst regeneration [62,78]. Table 3 explains the catalytic conversion of glycerol to different chemicals which are beneficial to us. Numerous amount of studies were made by different researchers with different catalysts to produce value added chemicals.

Catalyst coking occurs when coke is formed on catalyst surface and blocks the pores that obstruct reactant contact on active sites. Coke is easily produced from consecutive oligomerization and aromatization reactions such as for acetaldehyde, acetol, acrolein, propionaldehyde, acetone and olefins [7,64,75]. When catalyst is poisoned, reactions that lead to the desired product and conversion would not take place. At the moment, it is still inaccurate to claim that crude glycerol contributes significantly to catalyst coking. This scenario depends on the type of glycerol catalytic transformation. Even when refined glycerol is employed, solid catalyst will deactivate and the catalyst activity could not last long [79]. Dehydration of glycerol to acrolein, for instance, witnessed a rapid catalyst deactivation although good product yield was achieved at the beginning when refined glycerol was applied [75]. Upon consuming crude glycerol, the effect is even worse as solid catalyst deactivates rapidly in the presence of impurities, organic materials and inorganic salts [11].

Hypothetically, catalyst regeneration is essentially required to ensure that the catalyst regains its activity. Hence, concerted efforts are focused on the study of catalyst regeneration [62]. Investigation of crude glycerol transformation to aromatic BTX and 1,2-propanediol displayed good catalyst activities up to 11 times [52] and 4 times [62] of catalyst reactivation, respectively. As expected, the catalyst activity dropped after that.

To overcome this, continuous catalyst regeneration or reactivation must be carried out. But for a continuous process, this is tricky and a waste of time as the reaction must be halted to give way for the catalyst reactivation. One approach to avoid ceasing the reaction process is to co-feed small amount of oxygen that can help suppress the side products and coke formation [75]. Encouraging results were reported on the conversion and selectivity, and can result in relatively longer lifespan of the catalyst [80]. Nonetheless there is no report proving that co-feeding oxygen can extend life of catalyst to more than a few days. More work should be geared up to overcome these weaknesses.

Another method that could curb the formation of coke is by raising the reaction temperature to above 650 °C as in the case of glycerol steam and dry reforming. Coke formation originates from disproportionation of CO, methane decomposition, hydrogenation of CO_2 and hydrogenation of CO reactions [81]. The disproportionation of CO, also identified as Boudard reaction, has become officious at temperatures less than 1000 K. In this reaction, formation enthalpy of CO_2 is higher than CO but the formation entropy is lower. As a result, the overall Gibbs free energy change of formation of CO_2 by oxidation is almost constant regardless of the temperature [82]. This implies that at lower temperatures the equilibrium favours exothermic CO_2 and solid carbon formation. Coke formation from methane decomposition, hydrogenation of CO_2 and hydrogenation of CO reactions are mostly unlikely for temperature above 1000 K because the reactions are primarily affected by equilibrium limitation [83].

Nevertheless, despite the effort to minimize coke formation via co-feeding with oxygen and manipulating reaction temperature, the fact is the catalysts are still thermally unstable and not robust yet. Hence, superior robust catalyst with longer lifespan and more attractive product selectivity must be produced. Besides ensuring catalyst to be perfectly designed to favour the desired chemical yield and able to last longer, the extreme alkalinity or acidity properties must also be carefully considered as it can cause severe corrosion in reactor [75]. This effect may not be seen in the lab scale, but can devastatingly contribute towards commercial scale as stainless steel reactors are often employed. Awareness and precaution upon using highly alkali and acidic catalyst must be taken. Reactor wall thickness must be measured periodically based on National Association of Cor-

Table 3. Important value-added chemicals derived from catalytic conversion of glycerol.

Chemical formula	Chemical name	Glycerol Transformation Process	Name of the Catalyst	Refs.
H_2	Hydrogen	Reforming	Ni/AC, Ni-La-Ti,	[63,64,99]
$C_3H_6O_2$	3-hydroxypropanal	Dehydration	Heterogeneous catalysts	[76,100]
$C_3H_6O_2$	Hydroxyacetone	Dehydration	Heterogeneous catalysts, Au	[76,101]
$C_3H_6O_3$	Glyceraldehyde	Oxidation	Heterogeneous catalysts	[11,76,102]
$C_3H_6O_3$	Lactic acid	Oxidation	Bifunctionals catalyst, Cu-Pt/AC	[103-105]
C_3H_4O	Acrolein	Dehydration	silicoaluminophosphate SAPO-40, ZSM-5 zeolite, MWW-type catalysts,	[7,87,106,107]
$C_3H_4O_2$	Acrylic acid	Oxidation	ZSM-5 zeolite, mixed oxide catalysts	[7,108]
$C_3H_8O_2$	1,2-propanediol	Hydrogenolysis	Cu-Ni, Pt-modified Ir-ReOx/SiO2, Pt/ASA,	[8,109-112]
C_3H_5ClO	Epicholorohydrin	Halogenation	Multifunctional catalysts	[11,69,113,114]
$C_4H_6O_4$	Glycerol carbonate	Transesterification	Epoxide monomers, 1,8-diazabicycloundec-7-ene (DBU), natural clinoptilolite	[36,37,40,115,116]
$C_3H_6O_2$	Glycidol	Transesterification*	1,8-diazabicycloundec-7-ene (DBU)	[36,100,117]
$C_3H_6O_4$	Glyceric acid	Oxidation	Bi-promoted Pt/NCNT, Cu-Pt/AC, 1% Au/charcoal or 1% Au/graphite	[9,38,105]
$C_3H_6O_3$	Dihydroxyacetone	Oxidation	Au, Sn-silica nanotubes, Bi-promoted Pt/NCNT,	[2,9,60,101]
$C_3H_4O_5$	Tartronic acid	Oxidation	Pt, Bi-Pt	[32]
$C_3H_2O_5$	Mesoxalic acid	Oxidation	C-Pt-Bi	[30]
$C_3H_4O_3$	Pyruvic acid	Oxidation	Pb-Pt/AC	[118]
$C_3H_4O_4$	Hydroxypyruvic acid	Oxidation	Bi-Pt (acidic)	[32]
C_3H_6O	Allyl Alcohol	Hydrogenolysis	-	[110,119,120]
C_3H_6O	Acetone	Hydrogenolysis	Heterogeneous catalysts	[76]
C_3H_6O	Propanal	Hydrogenolysis	Pd/α-Al_2O_3	[121]
C_3H_8O	2-Propanol	Hydrogenolysis	Ni	[93]
C_3H_6	Propylene	Hydrogenolysis	MoO_3-modified Ni_2P/Al_2O_3, HZSM-5, Al/ZSM-5, Ca/ZSM-5, Cr/ZSM-5, Cu/ZSM-5, Li/ZSM-5, Mg/ZSM-5 and Ni/ZSM-5	[54,55,110]
C_3H_8	Propane	Hydrogenolysis	Pt/H-ZSM5	[53]
$C_4H_8O_2$	Dioxane	Condensation	-	[11]
$C_3H_6O_2$	Dioxalane	Condensation	-	[11]
RCO_2R'	Glycerol esters (e.g.: Monoacetin, diacetin and Triacetin)	Esterification	Heterogeneous catalysts	[3]
R–O–R′	Glycerol ether (e.g.: Mono-, di-, tri-tertiary butyl glycerol ether)	Etherification	Resin catalyst	[3,122]

rosion Engineers (NACE) International standards, which are briefly discussed in the subsequent section.

3.3 Reactor Consideration?

Selection of reactor directly correlates with the process and catalyst properties. Highly acidic or alkali catalyst may negatively affect the internal parts and wall of a steel reactor in the form of corrosion [84,85]. Heavy corrosion may impair the functioning of reactor parts and reduce their lifetime. This, in turn, would increase the shut-down periods of reactors for maintenance and repair work, with a corresponding rise in operating cost.

If such extreme catalyst could not be avoided, the manufacturing processes will need plastic-lined or glass-lined steel equipment for its reactors. Highly permeable chemicals, especially at high temperatures and high pressures require plastic-lined steel equipment that has a liner with the lowest permeation and diffusion rates while providing a reasonable lifetime and commercial success [86]. The CAPEX for preparing for such reactor and its related infrastructure will be tremendously high. Hence, careful consideration must be planned at the early state of research regarding the process technology, catalyst and operating process parameter.

Technology of catalytic transformation of glycerol to chemical also involves not just two or three reactors, but a number of other vessels and unit operation. The process, catalyst and product will dictate the type of reactors. Hence, study of comparison of reactor for specific process should be performed such as the one conducted by Nomanbhay but he only focused on glycerol pyrolysis [70]. The efforts to study available reactors for glycerol thermochemical reaction should be extended to other types of process, such as steam reforming or carboxylation.

Subsequently, process optimization of the technology involving the reactor and scaling up should be performed. Optimization is key fundamental in the way to reduce the impact of feedstock variability and impurities.

3.4 In-depth Knowledge on Reaction Mechanism and Thermodynamics

Strong and deep comprehension on what is happening in the complex reaction network of this biomass is imperative. Multiple reactions take place simultaneously in a fraction of time, some which are formed within split second and followed by a series of other reactions. Multiple products are temporarily formed and vanished to a more stable product. Henceforth, the understanding of the reaction mechanism of a process is very critical and this directly relates to the catalyst properties. A glycerol dehydration reaction direction is decided by the strength of acid as well as type of acid (Lewis or Brönsted) within the catalyst surface [76]. Products from glycerol dehydration for a steam reforming at 400 °C could be hydroxyacetone if the hydroxyl group of glycerol reacts with Lewis acid site; or 3-hydroxypropanal should hydroxyl group favours Brönsted acid site. But, it has been reported that 3-hydroxypropanal is readily converted to acrolein, a more stable compound, via subsequent dehydration reaction. Earlier before, Corma reported that glyc-

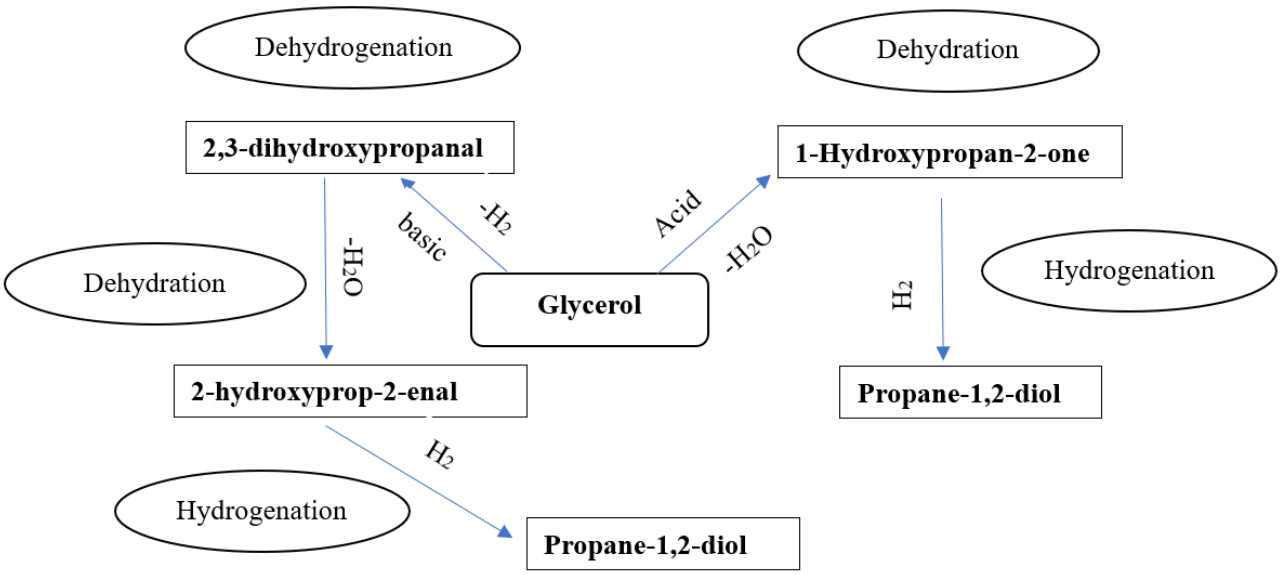

Figure 3. Reaction Mechanism for production of 1,2-Propanediol (1,2-PDO) [94].

erol dehydration at temperature 350 °C and 500 °C takes place in two pathways and declared that 66% will be directed to the formation of acetol and 33% towards acrolein. Transformation to acetol and its sub products occurred due to the glycerol molecule central alcohol function removal [77]. Other complex reaction network postulations were discussed by [22,76,87].

Besides reaction mechanism knowledge, thermodynamics of each reaction in the complex reaction network is substantially imperative and could provide precious information. Adhikari in his study of glycerol steam reforming to hydrogen revealed that the thermodynamics investigation heavily depends on process variables (pressure, temperature and ratio of reactants) [88]. Cheng and co-workers studied the thermodynamic analysis of glycerol-steam reforming in the presence of CO_2 or H_2 as carbon gasifying agents which demonstrated that existence of co-feed directly affects the product selectivities based on the temperature and pressure [89]. Other thermodynamic researches include thermodynamic feasibility of glycerol dry autothermal reforming [90], thermodynamic analysis of different carbon deposits from oxidative steam reforming of glycerol to produce hydrogen [91] as well as the thermodynamic investigation of glycerol conversion to light olefins [83]. An important point to note is that, all the thermodynamic analysis conducted was performed without catalyst. Hence, a more advanced study involving specialized catalytic thermodynamic analysis for glycerol conversion to chemicals must be developed.

Figure 3 represents the production of 1,2-Propanediol (1,2-PDO) from glycerol. Under hydrogenolysis conditions, it is the most possible reaction pathway. For glycerol hydrogenolysis, metal-acid bifunctional catalysts have been identified as the most successful.

Co-etherification with isobutene and tert-butanol improves glycerol conversion. Figure 4 displays the reaction mechanism. The etherification of glycerol with isobutene or tert-butanol yields tert-Butyl glycerol ethers, which are useful fuel additives. Isobutene and glycerol both react well to the amphiphilic tert-butanol. As

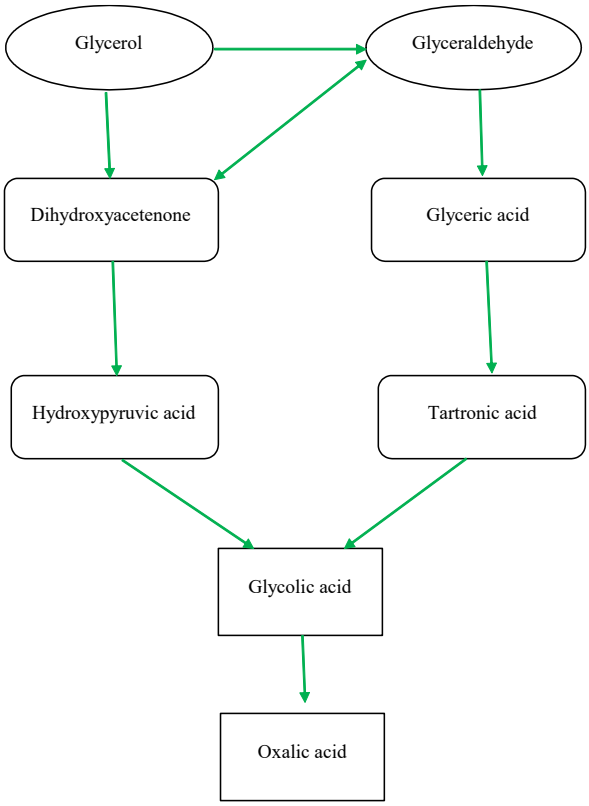

Figure 5. Reaction pathway from glycerol [96].

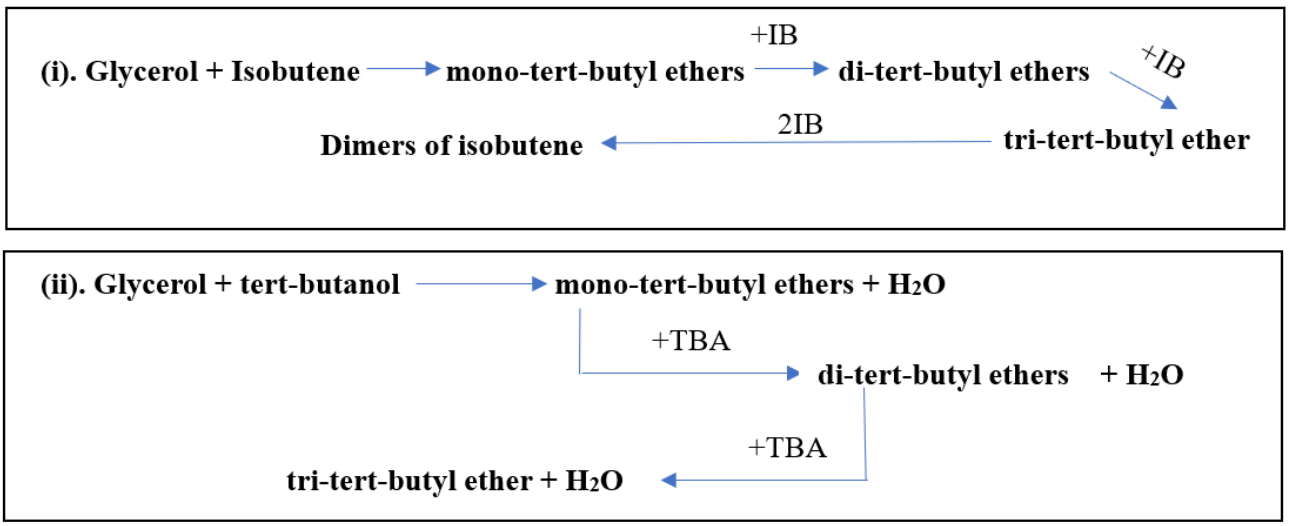

Figure 4. Reaction mechanism for glycerol etherification with isobutene and with tert-butanol [95].

tert-butanol is added to a glycerol-isobutene reaction, it increases the isobutene concentration in the glycerol and hence the reaction rate. In glycerol etherification, replacing a portion of tert-butanol with isobutene could transfer the reaction to polysubstituted ethers while also reducing the amount of water formed. Overall, the addition of isobutene could increase glycerol conversion and produce more polysubstituted ethers. Acid catalysts, such as resins, zeolites, and other materials, can catalyse both reaction mechanisms under identical conditions.

Alexander Luis Imbault and his co-workers studied on converting glycerol into carbonyl compounds. Figure 5 shows the pathway for conversion of glycerol. Glycerol conversion reactions in the gas phase using bifunctional hierarchical zeolite-supported bi- and tri-metallic catalysts to produce allyl alcohol was studied by Andrii Kostyniuk. Figure 6 illustrates the reaction pathway by using CsFeMo/HZSM-5 catalysts for glycerol conversion to allyl alcohol and other reaction products. The dehydration and transition hydrogenation process was used to extract allyl alcohol directly from glycerol over the simple sites of the CsFeMo-ZSM-5 catalyst. On Lewis and Brönsted acid sites, hydroxyacetone and acrolein activity took place at the same time. It was discovered that the addition of Cs to FeMo-ZSM-5 inhibited all reactions.

In short the chemistry of glycerol conversion must be properly understood via reaction mechanism and thermodynamics feasibility. From the knowledge of this glycerol complex reaction network, catalyst can be tailor made to fulfil the demand for the desired reaction pathway.

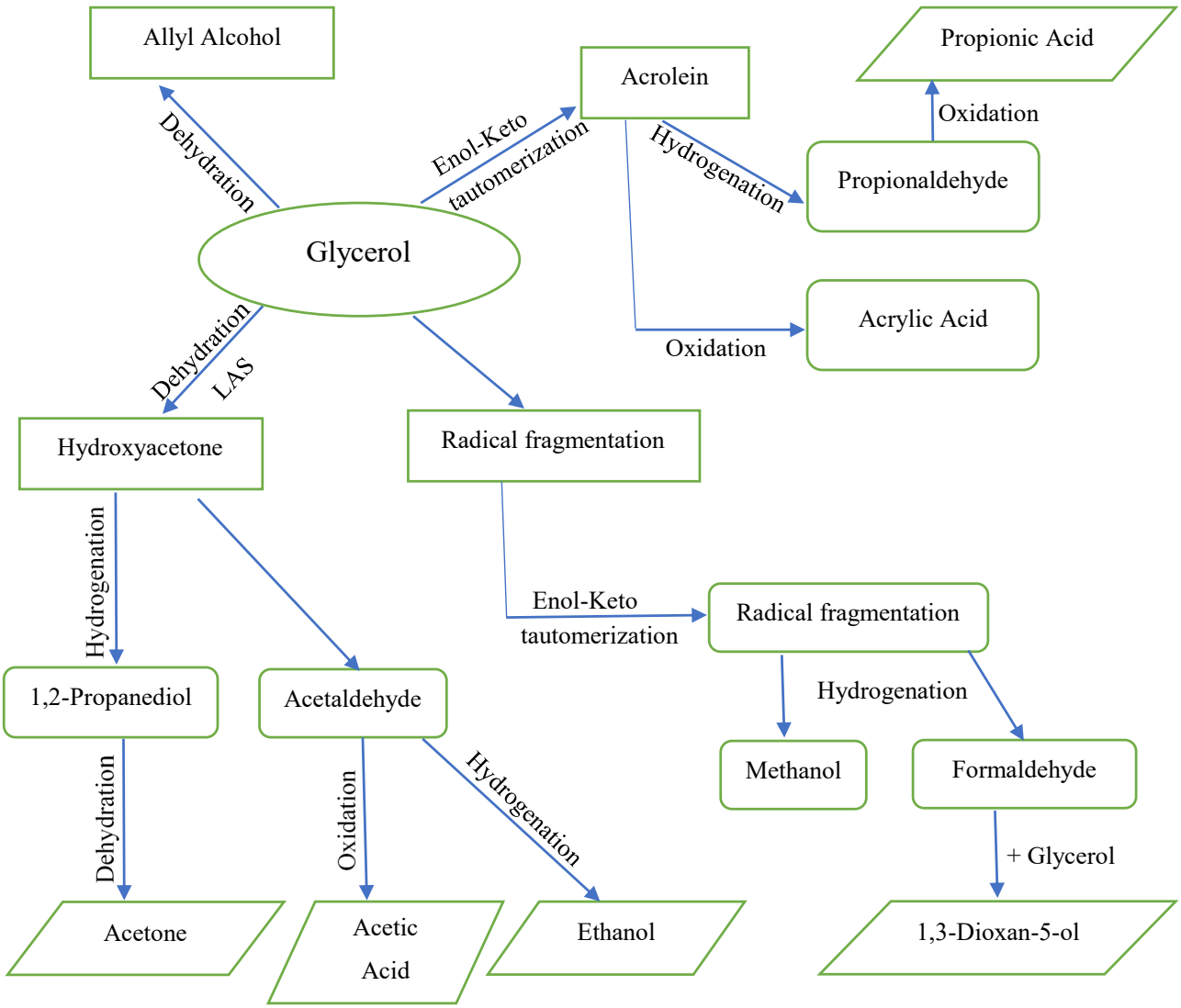

Figure 6. Reaction pathway by using CsFeMo/HZSM-5 catalysts for conversion of glycerol to other products [123]

3.5 Commercial Viability of the Overall Process

All knowledge and information discussed earlier will not be sufficient to run a profitable business. The overall comparison of feasibility, cost viability, exergy for specific products and processes should be carried out. However, before a specific process is chosen, it is essential to make detailed comparison between all the available processes. A brief but good comparison of reactors for pyrolysis were carried out that include the variety of percentage product yield [70]. Although most of the comparisons dwell between lab scale researches, the input provides great indication on what really works. Most of the current methods of utilization of crude glycerol are only able to uptake small volumes of the waste glycerol and the real costs of its utilization are uncertain or not carried out. On top of that, percentage yield, the energy/mass, product/cost and others must also be considered, not to mention the recovery cost as well. The Engineering Procurement and Construction (EPC) would not be a tough task if all the above discussed aspects are well established and covered. Another perspective to consider is the exergoeconomic and exergoenvironmental of glycerol conversion into value-added chemicals. It is imperative to focus into the reactor and process development holistically. As up to this point, not much work on the exergoeconomic and exergoenvironmental of glycerol transformation have been reported, apart from that of Aghbashlo and co-workers, where they analysed the solketal synthesis via glycerol ketalization with acetone in the presence of ethanol as co-solvent and Purolite PD206 as catalyst [92].

An established chemical plant such as propylene glycol that is processed via hydrogenolysis is good because cheap catalyst is employed but at the same time there is always room for improvements, especially in the technological, energy and cost perspective. The production of propylene glycol still requires ex-situ hydrogen supply [75]. Freitas et al. investigated a continuous reaction pathway, without external hydrogen, for glycerol transformation to propylene glycol via dehydration to acetol, with simultaneous reforming to H_2 and CO_2. The H_2 formed from the reactions itself was used for the hydrogenation of acetol to propylene glycol using $CuNi/Al_2O_3$ and CuNi/ZSM-5 [8]. In a separate study, Maglinao and co-workers converted crude glycerol to propylene glycol in a batch pressure reactor and Raney nickel catalyst, without having to supply hydrogen. Highest propylene glycol of about 33% was attained when 6 wt% of nickel based catalyst was used at glycerol : water ratio of 1 to 1 for 45 minutes at 230 °C [93].

Catalytic reactor processing and scaling up investigations need to be beefed-up. A solid heterogeneous catalyst for these processes integrated with continuous processing technology is expected to gain wider acceptance in the future due to its potential effectiveness and efficiency. While there are potential benefits that the solid heterogeneous catalyst can offer, issues related to the low catalytic activity, leachates, reusability and regeneration should be addressed and emphasized in the future research in order to ensure sustainability of the process. The reaction kinetics and also thermodynamic feasibility of glycerol transformation need to be addressed as well.

Other associated matters for the production of value-added chemicals, such as logistic, economic analysis and pilot study, will soon be emerged alongside with the technological investigation.

4. Perspectives

Both refined and crude glycerol can be catalytically converted to value-added chemicals. The key issue, though, is the general viability of the process. While numerous reports stated that a good high percentage yield of chemicals was obtained, which was mainly at the lab scale level, it is not guaranteed that a comparable outcome can be obtained. Figure 1 depicts the five crucial issues that must be tackled in order to pursue a more practical catalytic transition of glycerol to value-added chemicals. Each factor is determined by the nature and robustness of the catalyst. A great catalyst with a longer lifetime and reasonable operation is a competitor with a better risk of industrial productivity. The development of this advanced catalyst will guide the production of reactant types, reactor technologies, reaction mechanisms and thermodynamics, as well as the prediction of overall process commercial viability.

5. Conclusion

Conversion of glycerol to value added chemicals are still in pursuit for commercial success. Only a few of the available technologies are readily available for commercialization for a few chemicals. There are still huge opportunities for exploration of the catalytic transformation of glycerol to its derivatives. Modelling or simulation of proposed reaction schemes has been scarce. Thus, besides experimentally

tweaking, testing and optimizing the process, it is essential to study the modelling and simulation aspect as well.

Taking into consideration of the above, more investigations need to be carried out for improvement in the area of robust and effective catalyst (catalysis engineering), reaction engineering and reactor development, reaction kinetics, process optimization, scaling up and pilot plant development in the glycerol transformation to value added chemical context. The tensions in the diminishing price of glycerol market worldwide have amplified more needs to establish convincing routes of obtaining green chemicals. Hence, the transformation of glycerol is seen to be a more sustainable and environmentally friendly process. Therefore, concerted research efforts should be aggressively geared towards it.

Acknowledgments

The authors would like to thank Universiti Teknologi Malaysia's Collaborative Research Grant (4B485) and Ministry of Higher Education Malaysia (MOHE) for the financial support through Fundamental Research Grant Scheme (FRGS/1/2020/TK0/UTM/02/97).

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Selected and Revised Papers from International Conference on Sustainable Energy and Catalysis 2021 (ICSEC 2021) (https://engineering.utm.my/chemicalenergy/icsec2021/) (School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 16-17th February 2021) after Peer-reviewed by Scientific Committee of ICSEC 2021 and Peer-Reviewers of Bulletin of Chemical Reaction Engineering & Catalysis.
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